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I. Peltier Entropies of Gas Electrodes in Carbonate Paste Electrolytes

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ABSTRACT

Standard Peltier entropies for the reactions

$$\tfrac{1}{2}\,O_2 + CO_2 + 2e^- \rightarrow CO_3^{--}$$

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{--}$$

in molten carbonate paste electrolytes at 1000°K have been determined from thermogalvanic measurements. The results are −217 and −118 J/mole°K, respectively. No dependence on electrolyte composition is observed. The reversible part of the Peltier entropy for the oxygen electrode reaction is estimated from thermodynamic data and reasonable agreement with the experimental results is found. It is concluded that the main contribution to the Peltier entropy arises from the transition from gaseous to liquid state, whereas the transfer entropies of the ionic species are of minor importance.

In power-producing electrochemical cells, heat is liberated from the electrode reactions and the irreversible losses. In most cells working on solid- or liquid-state reactants, the entropy of reaction will in practice be of minor importance compared to the contributions from ohmic resistance and electrode polarization. However, if the electrode reactions have a net consumption or production of gaseous components, the entropy change will be considerable, due to the transition of state, and has to be taken into account. On the basis of the over-all heat evolved in a single cell during load, the temperature distribution in fuel cell batteries has been treated (1-3), but so far little attention has been paid to the single electrode heat balance and temperature gradients inside single cells caused by nonsymmetrical heat evolution at cathode and anode.

The heat evolved at a reversible electrode is determined by the Peltier entropy of the electrode reaction, which may be found from thermogalvanic measurements. Previously, the Peltier entropies of high temperature gas electrodes in ionic conducting oxides like ZrO_2 (4) and ThO_2 (5) have been investigated, and we have reported some preliminary results for carbonate electrolytes (6), which still left some uncertainty about the dependence on temperature and carbonate composition.

In this paper, the Peltier entropies of the $O_2 + CO_2$ and the $CO + CO_2$ electrode are determined. In part II of this paper, the heat evolved at the electrode during the irreversible passage of current is related to the Peltier entropies and some effects of the temperature gradients created are discussed.

Theory

For the thermogalvanic cell involving a mixture of molten carbonates

$$Pt(T)\,|O_2 + CO_2|Me_2CO_3|O_2 + CO_2|Pt(T + \Delta T) \qquad [A]$$

with the electrode reaction

$$1/2\,O_2 + CO_2 + 2e^- \rightarrow CO_3^{--} \qquad [1]$$

the Peltier entropy $\Delta S_P(O_2, CO_2)$ may be determined from the thermogalvanic force ΔTGF by the equation (7)

$$2\mathbf{F}\frac{\Delta TGF}{\Delta T} = \Delta S_P(O_2, CO_2) = \Delta S_P^{\circ}(O_2, CO_2) + R \ln p(O_2)\,\tfrac{1}{2}p(CO_2) \qquad [2]$$

where the standard Peltier entropy is given by

$$\Delta S_P^{\circ}(O_2, CO_2) = [S^{\circ}(CO_3^{--}) - 1/2S^{\circ}(O_2) - S^{\circ}(CO_2) - 2S^{\circ}(e^-)] + \Delta\hat{S} \qquad [3]$$

The first term in Eq. [3] is the reversible entropy of reaction, whereas $\Delta\hat{S}$[1] is the entropy of transfer corresponding to the homogeneous part of the thermogalvanic force, *i.e.*, the thermal diffusion potential in the electrolyte and the electrode leads.[2] $\Delta\hat{S}$ is composed of the transfer entropies of the species carrying the current according to

$$\Delta\hat{S} = t(CO_3^{--})\hat{S}(CO_3^{--}) - 2t(Me^+)\hat{S}(Me^+) - 2\hat{S}(e^-) \qquad [4]$$

These excess entropies of transfer arise from the fact that transported particles are not average particles but a selected ensemble, thus carrying an excess entropy, the transfer entropy (8). Compared to the equilibrium term in Eq. [3], involving a transition from gaseous to liquid state, the transfer term [4] is expected to be of secondary importance.

For the cell

$$Pt(T)\,|CO + CO_2|Me_2CO_3|CO + CO_2|Pt(T + \Delta T) \qquad [B]$$

having the electrode reaction

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{--} \qquad [5]$$

we obtain the expressions

[1] The entropy of transfer $\hat{S}$ is related to the transported entropy S^* used in Ref. (7) by the equation $\hat{S} = S^* - S$.

[2] It is noted that since the single electrode potential is not a measurable quantity, the numerical separation of the thermal emf into contributions from the homogeneous and heterogeneous transfer processes can only be performed on the basis of a convention.

Key words: thermocell, Peltier entropy, molten carbonate, gas electrodes.

$$2\mathbf{F}\frac{\Delta TGF}{\Delta T} = \Delta S_P(CO, CO_2) = \Delta S_P^\circ(CO, CO_2) + R\ln\frac{p^2(CO_2)}{p(CO)} \quad [6]$$

$$\Delta S_P^\circ(CO, CO_2) = [S^\circ(CO_3^{--}) + S^\circ(CO) - 2S^\circ(CO_2) - 2S^\circ(e^-)] + \Delta\hat{S} \quad [7]$$

where $\Delta\hat{S}$ is also determined by Eq. [4].

Subtracting [7] from [3] yields

$$\Delta S_P^\circ(O_2, CO_2) - \Delta S_P^\circ(CO, CO_2) = S^\circ(CO_2) - 1/2S^\circ(O_2) - S^\circ(CO) \quad [8]$$

which shows that Peltier entropies of different electrodes in the same media are related by well-known thermodynamic magnitudes, not involving single ion or transport properties.

When a cell similar to [B] contains an equilibrated mixture of "C-H-O gases" (such as reformed hydrocarbons), the only species of importance above the carbon deposition temperature are the gases H_2, CO, CH_4, H_2O, and CO_2 (9). Their equilibrium partial pressures are given by the reactions

$$H_2 + CO_2 \rightleftarrows H_2O + CO \quad [9]$$

$$K_s = \frac{p(H_2O)p(CO)}{p(H_2)p(CO_2)} \quad [10]$$

$$4H_2 + CO_2 \rightleftarrows CH_4 + 2H_2O \quad [11]$$

$$K_m = \frac{p(CH_4)p(H_2O)^2}{p(H_2)^4p(CO_2)} \quad [12]$$

The Peltier entropy of this cell can be found from simple thermodynamic equilibrium considerations for the isothermal cell

$$(a)\,Pt(T)|C\text{-}H\text{-}O|Me_2CO_3|O_2 + CO_2|Pt(T)\,(c) \quad [C]$$

The "C-H-O" electrode reaction is a superposition of CO, H_2, and CH_4 oxidation reactions. In the case of an equilibrated gas mixture, these reactions will be linear combinations of the CO equilibrium [5] and the gas phase equilibria [9] and [11]. The Peltier entropy for the mixed "C-H-O" electrode reaction can, therefore, be calculated from the temperature dependence of the emf on the basis of the CO electrode reaction [5] when the change in gas phase composition is taken into account.

$$\Delta S = 2\mathbf{F}\frac{dE}{dT} = \Delta S_P(O_2, CO_2) - \Delta S_P(C\text{-}H\text{-}O)$$

$$\Delta S = -\tfrac{1}{2}S^\circ(O_2) - S^\circ(CO) + S^\circ(CO_2) + R\ln[p(O_2)^{1/2}p(CO_2)]_c + R\frac{d}{dT}\left[T\ln\frac{p(CO)}{p(CO_2)^2}\right]_a \quad [13]$$

This yields in combination with [2] and [8]

$$\Delta S_P(C\text{-}H\text{-}O) = \Delta S_P^\circ(CO, CO_2) - R\ln\frac{p(CO)}{p(CO_2)^2} - RT\frac{d}{dT}\ln\frac{p(CO)}{p(CO_2)^2} \quad [14]$$

Equation [14] reduces to [6] for the pure CO, CO_2 cell [B]. The last two terms in [14] can be calculated from the equilibrium constants K_s and K_m and the corresponding standard reaction enthalpies ΔH_s° and ΔH_m° when C/H/O atomic ratios of the fuel gas are given. An example is given in part II of this paper.

Experimental

Figure 1 shows the experimental arrangements. The electrolyte, a rather stiff paste of 45 weight percent (w/o) Me_2CO_3 and 55 w/o MgO prepared by careful mixing of the dry powders, heating overnight at 750°C in an Al_2O_3 crucible, and subsequent grinding in an alumina ball mill, is pressed into an alumina tube at a temperature just above the melting point.

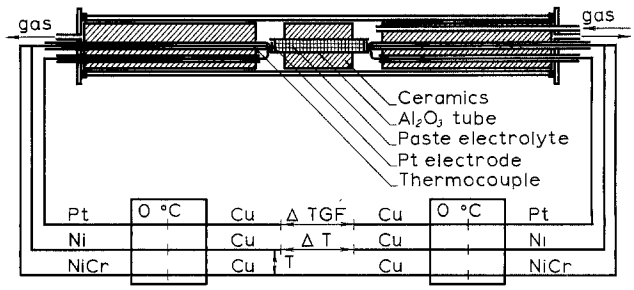

Fig. 1. Experimental setup for the determination of thermogalvanic forces in paste electrolyte.

The platinum electrodes are fixed at the end of the thermocouple protection tubes. During the initial heating of the oven, when the temperature had just passed the melting point of the electrolyte, the thermocouples were pressed against the electrolyte in order to ensure a proper electrode-electrolyte contact.

The gas mixtures were fed to the center of the oven and removed from both ends in order to avoid disturbance from CO disproportionation with associated carbon deposition in the colder parts when reducing atmosphere was applied. Furthermore, the gas volume and space time were reduced by ceramic plugs also serving as heat insulation between the two electrode compartments.

The oven is equipped with two separate bifilar heating coils supplied from voltage-stabilized transformers. The thermocouples are Ni/NiCr. The thermogalvanic force and the thermocouple voltage difference, ΔTEF, are recorded on a Servogor two-channel recorder connected to the outputs of the two Hewlett-Packard 3420 differential voltmeters. Utilizing the zero suppression feature of these instruments, full scale deflections of 100 μV for TGF and 10 μV for TEF are obtained on the recorder.

The experimental procedure is as follows: 45 min after a change of heating coil voltage, ΔTGF and ΔTEF are recorded for 15 min. Before and after the recording the temperature is read. The recordings are made in order to eliminate the effect of minor instabilities and drift due to voltage fluctuations in the mains. The voltage of the colder heating coil is then increased, thus creating a reverse temperature difference of approximately 15°C and a higher average temperature. After a 45 min equilibration period, the next set of readings is made. When the upper temperature limit of 900°C is reached, the measurements are repeated for decreasing temperature levels till the point of solidification, or in case of CO-CO_2 mixtures to the carbon deposition temperature of about 760°C (9).

Because of the thermocouple-electrode distance and the rather high thermal conductivity of the alumina tubes, the measured temperature differences are about 10% larger than the actual electrode temperature differences. To correct for this systematical error, the electrolyte is substituted by a Pt 10% Rh wire embedded in MgO and contacting the Pt electrodes. The thermoelectric force of this differential thermocouple is then determined using the procedure described above. A correction function is calculated from literature data.

Computation Procedure

The experimental procedure where only one set of ΔTGF, ΔTEF, and TEF readings is obtained at each temperature makes the calculation of the Seebeck

coefficient more complex than with the usual technique, where the Seebeck coefficient is calculated from the slope of a ΔTGF *vs.* ΔTEF plot at a fixed temperature. On the other hand, the method yields more information from the experimental effort, especially with respect to the temperature dependence.

The relation between the thermogalvanic force and the thermoelectric force of the thermocouples may be written as

$$\Delta TGF = \frac{\epsilon_E}{\epsilon_T'} [\Delta TEF + A(T)] \quad [15]$$

where ϵ_E and ϵ_T' are the Seebeck coefficients of the electrode and the apparent Seebeck coefficient of the thermocouples containing the systematical temperature error mentioned above. $A(T)$ is the temperature dependent offset error of the thermocouples.

If $\epsilon_E(T)$ and $A(T)$ are expanded in power series with respect to temperature

$$\epsilon_E = \sum_{i=0} e_i (T - T_o)^i \quad [16]$$

$$A = \sum_{j=0} a_j (T - T_o)^j \quad [17]$$

Eq. [15] may be rewritten as

$$\Delta TGF = \frac{1}{\epsilon_T'} \left[\Delta TEF \sum_{i=0} e_i (T - T_o)^i + \sum_{i=0} e_i \sum_{j=0} a_j (T - T_o)^{i+j} \right] \quad [18]$$

This equation shows how $\epsilon_E(T)$ may be determined from a multiple regression analysis with respect to ΔTEF $(T - T_o)^i$, i = 0, 1, 2, . . . and $(T - T_o)^l$, l = 0, 1, 2, . . . when $\epsilon_T'(T)$ is known.

$\epsilon_T'(T)$ may be obtained from the calibration experiments, where the thermogalvanic cell is substituted by a differential Pt/Pt 10% Rh thermocouple. In this case the Seebeck coefficient of Pt/Pt 10% Rh relative to ϵ_T' may be determined from Eq. [18]. Comparing this power series with literature data (10), also expanded in a power series, yields an analytical expression for ϵ_T' and allows the calculation of the Seebeck coefficients for the electrodes on the basis of Eq. [18].

Results and Discussion

In all cases, the colder electrode constituted the positive pole of the cell. Tables I and II give the experimental Seebeck coefficients and the standard Peltier entropies for the $O_2 + CO_2$ and the $CO + CO_2$ electrode. No temperature dependence is observed in any case. It is noted that the deviations between values obtained for identical electrolytes are larger than expected from the standard deviations calculated in the regression analysis. This indicates that the main error source is the reproduction from one experiment to another of electrode and thermocouple position inside the oven. Thus no significant dependence of the Peltier entropy on carbonate composition is found. This very small dependence of the Peltier entropy on the melt composition is expected, since the main entropy contribution originates from the transition from gaseous to liquid state, whereas the change with composition is in the order of mixing entropies.

Table I. Peltier entropy for the reaction $1/2\ O_2 + CO_2 + 2e^- \rightarrow CO_3^{--}$ in the temperature range 800°-1150°K

Electrolyte equimolar	mV/°K	Std dev, mV/°K	p_{CO_2}, atm	p_{O_2}, atm	ΔS_P^o, J/mole °K
$(Li,Na)_2CO_3$	−1.18	0.02	0.62	0.38	−220
$(Li,Na)_2CO_3$	−1.17	0.07	0.65	0.35	−218
$(Li,K)_2CO_3$	−1.14	0.01	0.65	0.35	−213
$(Li,Na,K)_2CO_3$	−1.14	0.02	0.67	0.33	−212
$(Li,Na,K)_2CO_3$	−1.20	0.02	0.65	0.35	−223
Average					−217

Table II. Peltier entropy for the reaction $2CO_2 + 2e^- \rightarrow CO + CO_3^{--}$ in the temperature range 1050°-1150°K

Electrolyte equimolar	mV/°K	Std dev, mV/°K	p_{CO_2}, atm	p_{CO}, atm	ΔS_P^o, J/mole °K
$(Li,Na)_2CO_3$	−0.66	0.02	0.50	0.50	−122
$(Li,K)_2CO_3$	−0.64	0.02	0.55	0.45	−120
$(Li,Na,K)_2CO_3$	−0.63	0.01	0.50	0.50	−116
$(Li,Na,K)_2CO_3$	−0.63	0.03	0.50	0.50	−116
Average					−118

As a check on the experimental values, the difference between the Peltier entropies for the two electrodes may, according to Eq. [8], be calculated and compared to literature data. Using the mean values in Tables I and II we obtain

$$S^o(CO_2) - \tfrac{1}{2}S^o(O_2) - S^o(CO) = \Delta S_P^o(O_2, CO_2) - \Delta S_P^o(CO, CO_2) = -217 + 118 = -99\ \text{J/mole°K}$$

compared to the value of −87.4 J/mole°K at 1000°K given in (11). This discrepancy is somewhat larger than expected from the standard deviations. The $CO + CO_2$ electrode is, in contrast to the $O_2 + CO_2$ electrode, very sensitive to minor changes in gas phase composition, which may be caused by convective mixing at the electrodes with partly decomposed gas from colder parts of the oven. Thus, the Peltier entropy determined for the $CO + CO_2$ electrode is less reliable and may be responsible for the deviation.

The reversible part of the Peltier entropy can be estimated on the basis of thermodynamic data. However, in order to obtain the entropy of the carbonate ion, it is necessary to know the contributions from vibration and rotation of the polyatomic ion. This difficulty may be avoided if, for example, the oxygen electrode reaction [1] is separated into the reactions

$$\tfrac{1}{2}\ O_2 + 2e^- \rightarrow O^{--} \quad [19]$$

$$O^{--} + CO_2 \rightarrow CO_3^{--} \quad \text{(solvation of } O^{--}\text{)} \quad [20]$$

From literature data the entropies of alkali oxides in the liquid state have been estimated as a function of temperature (12). Distributing the entropy equally among the ions and neglecting the mixing entropy, we obtain for an equimolar mixture of Li_2O and Na_2O at 1000°K the value

$$S^o(O^{--}) = (152 + 204)/6 = 59\ \text{J/mole°K}$$

For the combination of O^{--} and CO_2, Andersen (12, 13) has determined the free energy and entropy change in different carbonate melts. Using the value for $(Li, Na)_2CO_3$ gives

$$\Delta S^o(2\,O) = -126\ \text{J/mole°K}$$

which yields the estimate on the entropy of the carbonate ion in the liquid state

$$S^o(CO_3^{--}) = \Delta S^o(2\,O) + S^o(CO_2) + S^o(O^{--}) = -126 + 269 + 59 = 202\ \text{J/mole°K}$$

The transported entropy, $S^*(e^-)$, of the electron is calculated from the absolute thermoelectric force of Pt at 1000°K (10)

$$S^*(e^-) = S^o(e^-) + \hat{S}(e^-) = 17.1\ 10^{-6}\ 96{,}500 = 1.65\ \text{J/mole°K}$$

The reversible part of the Peltier entropy is now calculated as

$$\Delta S_{P,rev}^{\circ}(O_2, CO_2) = S^{\circ}(CO_3^{--}) - \tfrac{1}{2} S^{\circ}(O_2) - S^{\circ}(CO_2) - 2S^{\circ}(e^-) \simeq 191 \text{ J/mole°K}$$

which is rather close to the experimental Peltier entropy of −217 J/mole°K. The uncertainties introduced by the assumptions made above may readily account for the discrepancy. Thus, as expected the entropies of transfer only constitute a minor part of the Peltier entropies of gas electrodes in molten carbonates.

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LIST OF SYMBOLS

E	electromotive force (V)
$\mathbf{F}$	Faraday constant (C/mole)
ΔH	enthalpy of reaction (J/mole)
p	partial pressure (atm)
t	transport number
T	temperature (°K)
TEF	thermoelectric force (V)
TGF	thermogalvanic force (V)
S	entropy (J/mole°K)
ΔS_P	Peltier entropy (J/mole°K)
S^*	entropy of transported species (J/mole°K)
$\hat{S}$	excess entropy of transported species (J/mole°K)
ϵ	Seebeck coefficient (V/°K)
K	equilibrium constant

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Single Electrode Heat Effects

II. Single Electrode Heat Evolution

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ABSTRACT

The heat evolution at a single irreversibly working electrode is treated on the basis of the Brønsted heat principle. The resulting equation

$$\frac{dQ}{dt} = \left(T\frac{\Delta S_P}{n\mathbf{F}} + \eta \right) i$$

is analogous to the expression for the total heat evolution in a galvanic cell with the exception that $-\Delta S$ is substituted by the Peltier entropy, ΔS_P, of the electrode reaction. η is the overvoltage at the electrode. This equation is applied to a high temperature carbonate fuel cell. It is shown that the Peltier entropy term by far exceeds the heat production due to the irreversible losses, and that the main part of heat evolved at the cathode is reabsorbed at the anode. Finally, effects like thermal corrosion, caused by internal temperature gradients, are discussed.

Most treatments of heat effects in galvanic cells are based on the over-all heat evolution calculated from the reversible heat evolution, $-T\Delta S$, and the polarization losses. So far, little attention has been paid to the single electrode heat evolution. In galvanic cells working on solid- or liquid-state reactants and products, the main heat evolution is caused by the polarization losses, whereas in most fuel cells involving a net consumption of gaseous components, the single electrode reactions contribute considerably to the heat evolution at moderate loads. They may give rise to rather large temperature gradients inside the cell. In porous gas diffusion electrodes, temperature gradients may cause convection in the electrolyte film through gradients in

Key words: heat evolution, molten carbonate fuel cells, Peltier entropy, thermal corrosion.